# Mostly Nonuniformity Issues in Thin-Film PV

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## ABSTRACT

CdTe photovoltaics often exhibit strong fluctuations in electronic properties on a mesoscale level that originate from relatively weak microscopic fluctuations in material structure such as grain size, chemical composition, and film thickness. Amplification comes from the fact that electronic transport through potential barriers is exponentially sensitive to the local parameter fluctuations. These effects create new phenomena and establish the physics of large-area, thin-film devices as a distinctive field of its own, quite different from that of microelectronics. Our understanding suggests the methods for improvement the device performance and stability.

## 1. General review of UT activities

In polycrystalline thin-film PV, the University of Toledo has major efforts in CdTe-based materials and cells through the Thin Film Partnership Program and also through the High Performance PV Program. In this paper we provide some highlights of the Thin-Film Partnership activities. Space limitations prevent meaningful discussion here of our HiPerfPVactivities which include efforts on CdZnTe and CdMnTe alloys, transparent back contacts and tunnel junctions, and involve collaborations with First Solar and IEC.

## 2. Nonuniformities in thin-film PV

CdTe photovoltaics exhibit strong fluctuations in parameters of nominally identical devices. For example, it is typical to observe noticeable (~10%) experimental differences between cells ~1 cm apart on the same substrate (Fig. 1). If we imagine a typical 1x50cm linear cell in a terrestrial PV module as composed of a large number of smaller, slightly different cells, it becomes obvious that the latter will interact forcing lateral currents and building local charges. Thus the original linear cell turns out to be laterally nonuniform and there are losses related to the nonuniformity.

Physically, the nonuniformity originates from relatively weak local fluctuations in the materials parameters such as grain size, chemical composition and film thickness translate into strong fluctuations in the device electronic properties. The amplification comes from the fact that electronic transport through the potential barriers is exponentially sensitive to the local parameter fluctuations in both the temperature-activated and tunneling modes. Indeed, for a barrier of height $V_B$ and width $a$, the corresponding barrier transmission probabilities, $\exp(-V_B/kT)$ and $\exp\left(-2a\sqrt{2mV_B}/\hbar\right)$ typically have exponents much greater than one. Hence, their relatively small variations cause significant effects. The barriers are associated with the device junctions (p-n, n-TCO, and p-metal) and grain boundaries. For example, the ideal diode model

$$j = j_0\left\{\exp\left[\frac{e(V-V_{oc})}{kT}\right]-1\right\}, \tag{1}$$

predicts strong current fluctuations when $V_{oc}$ fluctuations exceed $kT$.

Experimentally, the nonuniformities are often masked by low resistance contacts. To circumvent this masking effect, the nonuniformities are best studied either in unfinished devices (without metal contact), in devices with intentionally high resistance contacts, or via processes that are relatively independent of metal contacts, such as charge carrier recombination or collection.

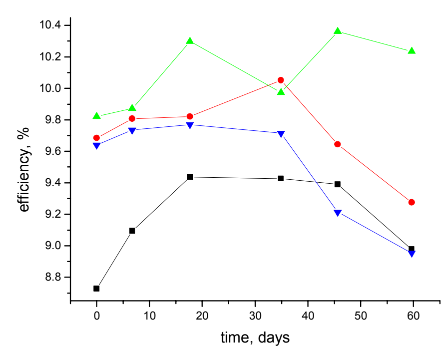


Figure 1. Typical Light-induced degradation of 4 nominally identical cells on the same substrate.

The available data (for an extended review see [1]) typically represent device mapping by either direct electrical measurements or more sophisticated techniques, such as optical-beam-induced current (OBIC), electron-beam-induced current (EBIC), and scanning-tunnelling microscopy (STM). For example, local Voc shows drastic variations ranging from 0.2 to 0.7 V between different grains as detected by STM for a $Cu(In,Ga)Se_2$ [2]. For similar devices, OBIC revealed microregions of reduced efficiency [3]. For CdS/CdTe cells, OBIC [4, 5] and EBIC [6,7,8] showed strong inhomogeneities dependent on post deposition treatments with length scales ranging from microns to millimeters. Time-resolved PL revealed variations in recombination lifetime, by a factor of two to three across one cm distances [9]. PL mapping [10] showed considerable nonuniformities on a large (~ 1 mm) scale whose topology depends on the excitation laser-beam power. Nonuniform degradation (also obvious from Fig. 1) in CdTe cells was noticed in Refs. [11] and [12]. In the recent work [13] it was observed that lateral nonuniformity causes divergence in the low light fluctuations of photovoltaic parameters.

The explanation of the lateral fluctuations effects lies in the device diode nature and in the presence of the resistive electrode. The weak (low $V_{oc}$) microdiodes are exponentially significant in accordance with Eq. (1). This is reflected in the equivalent circuit of Fig. 2. The microdiode size is of the order of the nonuniformity length scale *l*. The effects of nonuniformities depend on the relationship between the nonuniformity length scale *l* and the screening length ([14])

$$L(u) = \sqrt{u/\rho\, j_0}\,, \qquad (2)$$

where $u$ is the local fluctuation of electric potential, $\rho$ is the sheet resistance. The physical meaning of $L$ is that the fluctuation $u$ is supported by the resistive potential drop $j_0 L^2 \rho$. The length L varies over a wide range depending on the sheet resistance and photocurrent. For example, L~1mm under 1 sun illumination and u~kT/e, while under ambient room light (and correspondingly low current) L~1 m.

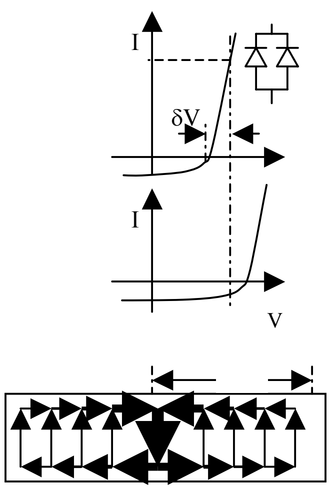


Figure 2. The equivalent two-diode circuit (inset) and I/V characteristics of the weak diode (shunting the current) and its more robust neighbour diodes. Because of the difference in the diode $V_{oc}$'s the weak diode finds itself under forward bias $\delta V$. The current distribution (bottom) shows the weak diode shunting effect by fat arrow.

As an illustration, shown in Fig. 2 is the open circuit electric potential mapping of a 10x10 cm2 sample of intentionally high resistive contact has a sheet resistance of 100 Ω/,. Side by side with the true shunt feature there are other profound fluctuations. When the contact is further developed to become a standard low resistance one (by depositing Al layer of ~100 nm) the potential fluctuations across the sample decrease down to the level of several mV. Based on the original fluctuation amplitude u ~ 0.025 V one can estimate the screening length $L$=1cm in Eq. (2). The current loss then becomes $\delta j \approx u/\pi L^2 \rho \approx 0.5 j_0$, that is *~50% of the current is lost due to lateral nonuniformity*. While the 50% figure per se may not be valid enough, we still can claims that it is dozens of percent of the current lost due to device nonuniformity. Hence, a great potential for the efficiency improvement. Note also that the above figure of 50% is consistent with the difference between the 17% efficiency record cells and typical 10-12% efficiency cells made in majority of labs. We suspect that the best cells overcome the nonuniformity problem by implementing techniques such as buffer layer, etc.

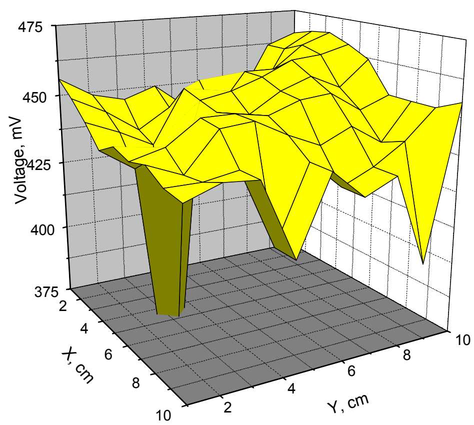


Figure 3. Electric potential variations of CdS/CdTe 10x10cm$^2$ sample with intentionally high resistive back contact (10 nm Cr) under low light of 0.01 sun. The main feature at X = 4 cm, Y = 3 cm represents a true shunt with voltage drop down to 0.05 V (cut off in the diagram).

Based on the above understanding, we would like to point toward several remedies, which, while keeping the semiconductor structure intact, can significantly reduce the device nonuniformity. As is seen from Fig. 2, the steeper the I/V curve in the forward bias region $V > V_{oc}$, the stronger the impact of a weak diode. Hence, increasing the series resistance will mitigate the detrimental effects on micrononuniformities. We verified the latter argument by numerically simulating the circuit of random diodes with series resistances added to each of the random diodes: a significant suppression of the electric current and electric potential lateral fluctuations was indeed observed.

The above prediction of the beneficial role of series resistance has two practical implications. First, the general quest for decreasing the device series resistance may not be justified in all cases. While this minimizes the ohmic loss, it can simultaneously promote losses due to nonuniformity effects. The analysis above shows that the series resistance should be carefully optimized to compromise between the ohmic and the micrononuniformity related losses.

The second implication has to do with buffer-layer effects, which, while proven generally positive, remain poorly understood. From the perspective of this paper, a beneficial effect of the buffer layer is that it adds series resistances to the weak diodes (or shunts). In understanding this effect it is crucial to take into account the characteristic micrononuniformity size $l$. The series resistance of the "clog" added by the buffer layer to a weak diode or shunt, $r_{bl} \propto l^{-2}$ is significant for small size nonuniformities, but may have no effect on nonuniformities of considerable lateral dimensions. Hence, the same buffer layer may or may not have positive impact on the device performance and stability, depending on details of the device technology affecting the micrononuniformity length scale. We believe that the buffer layer should be optimized based on the device uniformity characteristics.

Finally, we note that the above-discussed physics not only explains how nonuniformities are detrimental to device performance and stability, but also suggests a certain way of leveling them out. Namely, because the surface potential (local $V_{oc}$) under the light varies across a semiconductor film, electrochemical treatments sensitive to the electric potential will act differently at different spots. When properly chosen they should deposit clogs onto the weak diode spots while leaving the robust parts of the film practically intact, thus eliminating the most significant sources of nonuniformity effects. It is likely that in some cases such treatments have already been found in several cases by trial and error. In particular, that might explain why different pre-contact treatments, including weak etches and exposure to organics have a profound effect on device parameters. We believe that our present consideration provides the understanding to search effectively for the desired treatments. Work in this direction at UT is underway.

Our present consideration was mostly restricted to an elemental PV cell. Another closely related application should be mentioned where the concepts of nonuniformity and random diode arrays can be extremely important, which is the macroscopic circuitry of large area PV modules and their field arrays. A typical PV module is composed of a large number (~ 100) linear cells *in series*. Because of the cell diode nature, these series will be very sensitive to small variations in the cell parameters; hence, the problem of random diodes in series. Furthermore, in the field, photovoltaic arrays form more complex circuits where, for example, blocks of many modules in parallel are connected in series. Again, since the modules have slightly different characteristics, the latter systems will belong to the class of random diode systems. A relevant theoretical approach is being developed to understand their physics and optimize the design. We believe that enhanced understanding of the nonuniformity effects will help to improve thin-film device performance and stability in many applications.

**3. 14% sputtered cells with ZnO:Al as the TCO**

In other work, we have used sputtered ZnO:Al very successfully as a window layer for sputtered CdS/CdTe thin film solar cells. The Al-doped ZnO front contact was deposited on aluminosilicate glass by RF sputtering from a ZnO:$Al_2O_3$ target. The ZnO:Al film has ~95% average transmission in visible spectrum with ~3 ohm/square sheet resistance. The CdS and CdTe thin films were then deposited in a second chamber also by RF sputtering. Devices were completed with our usual vapor $CdCl_2$ treatment and with an evaporated Cu/Au back contact. The devices were tested at NREL, and an efficiency of 14% was confirmed for this all-sputtered CdS/CdTe solar cell. The improved performance over our previous best of 12.6% on Tec-7 glass (with $SnO_2$:F) is almost entirely due to higher current. The ZnO-based cell had $J_{SC}$ of 23.6 mA/cm$^2$ compared to 20.7 mA/cm$^2$ for the 12.6% cell. Other parameters of the 14% ZnO based cell are: FF = 73.25% and $V_{OC}$ = 814 mV. The test results are shown in Fig.4.

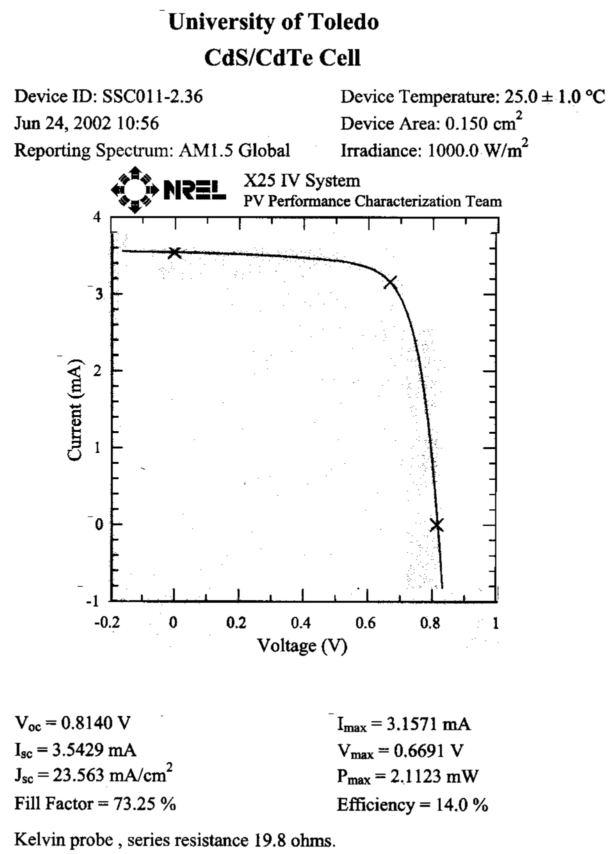


Figure 4. I-V test of recent 14.0% all-sputtered cell.

The quantum efficiency of this cell, with an as-deposited CdS layer of 0.13 µm, shows significant loss of response in the blue region due to the CdS absorption. We are currently studying how the CdS absorption can be reduced while maintaining high voltage and fill factor.

This work was supported by NREL under subcontracts NDJ-1-30630-02 (Ken Zweibel) and AAT-1-30620-09 (Martha Symko-Davies).

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